

ACTIVATED CAESIUM FLUORIDE – A RADIOTRACER STUDY

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Treatment of CsF with $(\text{CF}_3)_2\text{CO}$ in the presence of MeCN followed by thermal decomposition of the 1:1 adduct formed is one of the methods used to 'activate' CsF for use as a heterogeneous catalyst or reagent. We have compared ^{85}Kr adsorption at activated and untreated CsF and compared reactions of these materials with radiochemically labelled Lewis acids in order to quantify the activation effect.

Activated CsF has a B.E.T. surface area in the range $3.01 - 2.08 \text{ m}^2\text{g}^{-1}$ (95% confidence limits) compared with $0.3 \text{ m}^2\text{g}^{-1}$ for untreated CsF. Room temperature ^{18}F exchange between activated CsF and BF_2^{18}F or $\text{AsF}_4^{18}\text{F}$ is not observed, but reaction to give $\text{BF}_3^{18}\text{F}^-$ or $\text{AsF}_5^{18}\text{F}^-$ is rapid, and, in the case of $\text{BF}_3^{18}\text{F}^-$, complete. Uptake of $\text{AsF}_4^{18}\text{F}$ by CsF is smaller due to sintering. CsBF_4 prepared by this means undergoes no observable room temperature ^{18}F exchange with BF_2^{18}F , but ^{18}F exchange between BF_3 and BF_4^- in MeCN is rapid and complete. Uptakes of BF_2^{18}F and $\text{AsF}_4^{18}\text{F}$ by untreated CsF are far smaller, reflecting the smaller surface area; the extent of these reactions is comparable to that between activated CsF and the weaker Lewis acid SF_3^{18}F . No room temperature ^{18}F exchange is observed but ^{18}F and ^{35}S experiments enable surface adsorption and bulk reaction to be differentiated. 15% of the surface species are strongly adsorbed SF_5^- anions. The remainder are weakly adsorbed SF_4 molecules.